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Quantitative theory of a time-correlation function in a one-component glass-forming liquid with anisotropic potential

Edan Lerner, Itamar Procaccia, and Ido Regev
Department of Chemical Physics, The Weizmann Institute of Science, Rehovot 76100, Israel

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The Shintani-Tanaka model is a glass-forming system whose constituents interact via an anisotropic potential depending on the angle of a unit vector carried by each particle. The decay of time-correlation functions of the unit vectors exhibits the characteristics of generic relaxation functions during glass transitions. In particular it exhibits a stretched exponential form, with the stretching index β depending strongly on the temperature. We construct a quantitative theory of this correlation function by analyzing all the physical processes that contribute to it, separating a rotational from a translational decay channel. These channels exhibit different relaxation times, each with its own temperature dependence. Interestingly, the separate decay function of each of these processes is a temperature-independent function, and is shown to scale (exhibit data collapse) at different temperatures. Taken together with temperature-dependent weights determined *a priori* by statistical mechanics this allows one to generate the observed correlation function in quantitative agreement with simulations at different temperatures. This underlines the danger of concluding anything about glassy relaxation functions without detailed physical scrutiny.

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I. INTRODUCTION

The dynamics of glass-forming systems is typically investigated by measuring experimentally or computing in numerical simulations an appropriate correlation function of the density, the stress, a dipole moment, or any other physical quantity that can be used for this purpose. As the temperature of the supercooled liquid is lowered, the correlation functions exhibit more and more sluggish relaxation, and below some temperature become so slow to relax that accurate measurements of the relaxation time are no longer possible. In many glass-forming systems it appears [1] that a typical time- and temperature-dependent correlation function $C(T,t)$ can be well approximated by the so-called "stretched exponential" form,

$$C(T,t) \sim \exp\{-[t/\tau(T)]^{\beta(T)}\}, \tag{1}$$

where $\tau(T)$ is a temperature-dependent relaxation time and $\beta(T)$ is a parameter whose temperature dependence is usually poorly understood.

It is also common to fit the relaxation time $\tau(T)$ to a so-called Vogel-Fulcher form. i.e.,

$$\tau(T) = \tau_0 \exp[AT/(T - T_{\mathrm{VF}})], \tag{2}$$

where τ_0 is some microscopic time scale, A is a constant, and T_{VF} is a (finite) temperature where the relaxation time allegedly diverges. In recent work [2] we have put a question mark on the existence of finite-temperature divergences, proposing that in systems of point particles with soft potential (to be distinguished from, say, hard spheres) there is no divergence in the relaxation time except possibly at $T=0$. Indeed, in all experimental and simulational fits to Eq. (2) the temperature T_{VF} is rather far from the range of sampled temperature, and the extrapolation embodied in Eq. (2) is rather dangerous. Indeed, the theoretically claimed lack of a finite-temperature singularity was recently validated by careful reexaminations of the available experimental data (cf. [3,4]).

In this paper we demonstrate that also Eq. (1) can be misleading, since the relaxation process in glassy systems may very well be a composite process, including a number of relaxation channels. It is possible that each channel is characterized by a temperature-independent relaxation function, and it is only the relative weights of the various processes that result in an apparent temperature dependence of the relaxation function Eq. (1). This apparent temperature dependence is then read as a temperature-dependent $\beta(T)$. Of course, if Eq. (1) is put in doubt, then also the meaning of the fitted relaxation time $\tau(T)$ needs to be reevaluated. In particular, we recall that the temperature dependence of $\tau(T)$, whether Arrhenius or not, is used to classify glasses as "strong" and "fragile" in the Angell parlance [5]. Having doubts about the relevance of the fit functions may have interesting consequences on this issue as well.

The aim of this paper is to study these issues by analyzing in some detail the dynamics of the Shintani-Tanaka model [6] of glass formation. This model is very interesting since it consists of one type of point particles which interact via anisotropic interactions. As such it can mimic to some degree glass formers with hydrogen bonding, such as glycerol or water. As different systems may exhibit different ways of glassifying, albeit associated with some generic aspects of the phenomenon of glass formation, it pays to describe in detail the inhomogeneous states that develop naturally and to understand the role of a variety of dynamical processes that appear in various examples of glass transitions. We will attempt to expose how a number of distinct process come together to exhibit a seemingly complex phenomenology which can be understood in some detail. In particular, we examine separately the rotational and translational channels of relaxation, and how their relative contributions change upon decreasing the temperature. Importantly, we will show that the different channels are characterized by different relaxation times whose temperature dependence is not the same. Nevertheless the relaxation functions associated with these decay channels are temperature independent, as is shown below by data collapse. The paper culminates with a computation of a time-correlation function as a sum of the separate processes with *a priori* determined weights, in agreement with simulations at different temperatures. A similar decomposition and computation of the relaxation functions was achieved recently also for the model of a binary mixture with $1/r^{12}$ repulsion (see Ref. [10]).

A. Model and the numerical simulations

The model we employ here [6] has particles of mass m interacting via the potential

$$U(r_{ij},\theta_i,\theta_j) = \bar{U}(r_{ij}) + \Delta U(r_{ij},\theta_i,\theta_j), \tag{3}$$

where r_{ij} is the distance between the two particles i and j. The first term on the right-hand side of (3) is the standard isotropic Lennard-Jones potential $\bar{U}_{ij}=4\epsilon[(\sigma/r_{ij})^{12}-(\sigma/r_{ij})^6]$, whereas the anisotropic part of the potential is given by

$$\Delta U(r_{ij},\theta_i,\theta_j) = -4\epsilon\Delta\left(\frac{\sigma}{r_{ij}}\right)^6\left[h\left(\frac{\theta_i-\theta_0}{\theta_c}\right)+h\left(\frac{\theta_j-\theta_0}{\theta_c}\right) - \frac{64}{35\pi}\theta_c\right],$$

$$h(x) = \begin{cases}(1-x^2)^3 & \text{for } |x|<1,\\ 0 & \text{for } |x|\geqslant 1.\end{cases} \tag{4}$$

Here θ_i (θ_j) is the included angle between the relative vector $\boldsymbol{r}_{ij}\equiv\boldsymbol{r}_i-\boldsymbol{r}_j$ and a unit vector $\boldsymbol{u}_i$ ($\boldsymbol{u}_j$) (referred to below as "spin") which represents the orientation of the axis of particle i (j). The function $h((\theta-\theta_0)/\theta_c)$ (with $\theta_0=126°$ and $\theta_c=53.1°$) has a maximum at $\theta=\theta_0$, and thus θ_0 is a favored value of θ_i. Thus the anisotropic term in the potential favors structures of fivefold symmetry. The parameter Δ controls the tendency to fivefold symmetry, and therefore the frustration against crystallization. The units of mass, length, time, and temperature are m, σ, $\tau=\sigma\sqrt{m/\epsilon}$, and ϵ/k_B, respectively, with k_B being Boltzmann's constant. According to the numerical simulations presented in [6], for $\Delta<0.6$ this system crystallizes upon reducing the temperature. The ground state crystal has an elongated hexagonal structure with antiferromagnetic ordering of the spins $\boldsymbol{u}_i$. For $\Delta\geqslant 0.6$ the system fails to crystallize upon cooling, at least for the simulation times reported in [6].

The results reported below are based on our own simulations in two dimensions. In our work we used molecular dynamics simulations in the *NPT* ensemble. We employ the leapfrog algorithm [7] and Berendsen thermostat [7] with the parameter $\tau_T=5.0\tau$ and barostat with the parameter $\tau_P/\beta_T=50.0$ in the notation of [7], where β_T is the isothermal compressibility. We reproduced the dynamics described by [6]. The number of particles used was 4096 and the pressure was maintained at $P=0.5$ with periodic boundary conditions. All of the analysis described below was done using the data from these simulations. The time-autocorrelation function of interest was introduced in [6] in terms of the spins, in the form

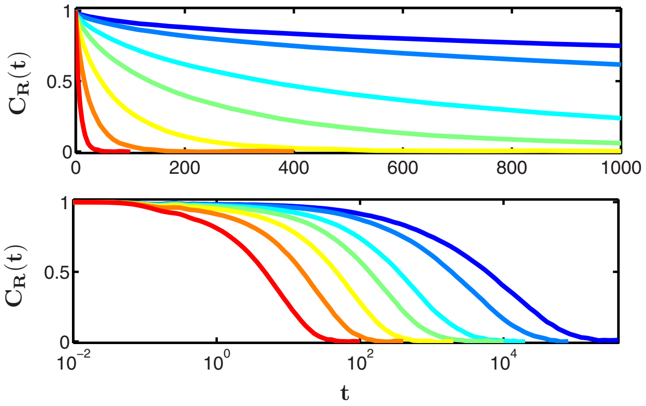

FIG. 1. (Color online) Relaxation function $C_R(t)$ as a function of linear time (upper panel), and of logarithmic time in the lower panel. The leftmost curve (in red) pertains to $T=0.4$ and in order to the right the temperatures are $T=0.3$, 0.25, 0.22, 0.20, 018, and 0.17. Note the extreme slowing down in this range of temperatures.

$$C_R(t) \equiv (1/N)\sum_i \langle \boldsymbol{u}_i(t)\cdot\boldsymbol{u}_i(0)\rangle. \tag{5}$$

Our own numerical results for this function are shown in Fig. 1. As is customary in the field [1], the measured correlation function was fitted in [6], to a stretched exponential form $C_R(t)\propto\exp[-(t/\tau_\alpha)^\beta]$. For $\Delta=0.6$ the relaxation is of Arrhenius form with a constant value $\beta\approx 0.95$ for $T>T_m=0.46$, but β was fitted separately for every temperature $T<T_m$, where it decreases with temperature. We stress that in general such a fit is not uniformly good at all times. The change of $\beta(T)$ with temperature destroys the possibility of data collapse. Indeed, even if we plot the correlation function (5) as a function of $t/\tau_\alpha(T)$, the functions do not superpose, as is demonstrated in Fig. 2.

Moreover, in [6] the relaxation times were fitted to a Vogel-Fulcher law $\tau_\alpha=\tau_0\exp[DT_0/(T-T_0)]$; below we will show that we can reconstruct the correlation function from

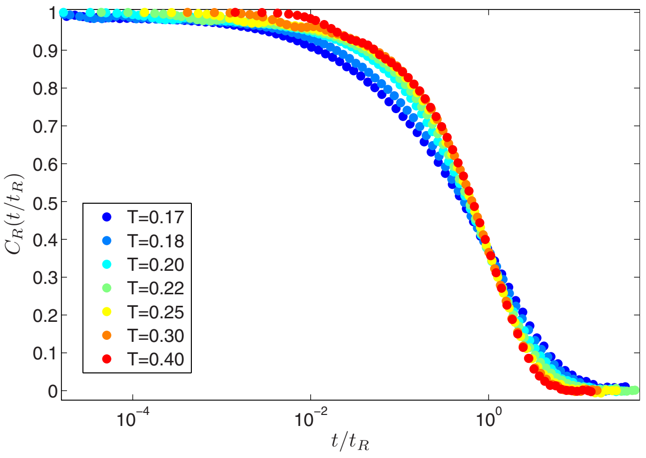

FIG. 2. (Color online) Relaxation function $C_R(t)$ as a function of rescaled time $t/\tau_\alpha(T)$. Note that the functions do not collapse on each other due to the change in functional form which is carried by $\beta(T)$.

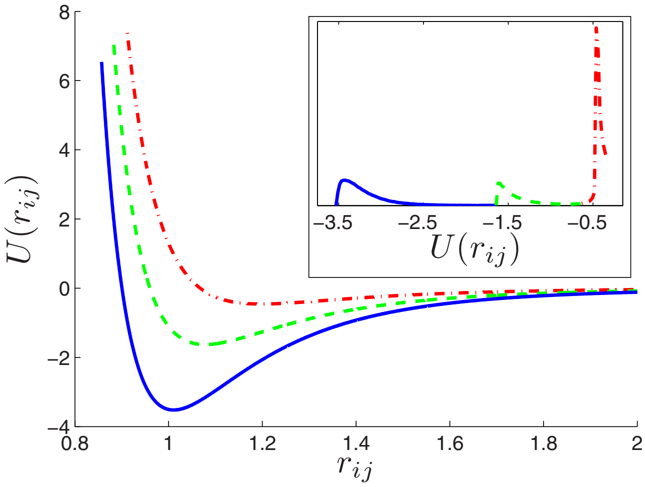

FIG. 3. (Color online) Potential curves for particle pairs with two spins, one spin, or no spin in favored position (blue continuous, green dashed, or red dashed-dotted line, respectively). Inset: the measured energies of particle pairs, falling in three distinct ranges with gaps between them.

elementary processes with temperature-independent relaxation functions (i.e., without needing to fit anything at different temperatures). As stated previously [2,8,10], the Vogel-Fulcher fit may be misleading in indicating a finite temperature where the relaxation time diverges. We do not expect any singularity here for any dynamical process for any $T > 0$. In the rest of this paper we describe how to represent the correlation functions seen in Fig. 1 in terms of the dynamical processes occurring in this system.

II. SUMMARY OF PREVIOUS RESULTS

To reconstruct the correlation function from elementary contributions we recall how statistical mechanics is built up for this system [11]. In Fig. 3 we present the three potentials between two particles, depending on the orientation of their spins relative to the interparticle vector distance: lowest in energy (blue continuous line) is the case for which both have a favored spin orientation; the middle (green dashed line) [high (red dashed-dotted line)] is the potential when one (none) of the spins is in a favored orientation. One sees that the minima of these potentials occur with significant gaps in their energies, allowing us to now measure the *average* energy of *pairs* of particles as a function of temperature. These averages fall in three distinct ranges, such that the range of variation of each energy is much smaller than the gaps between the energies (see inset in Fig. 3). We denote the three effective energies below as $2E_b$, $2E_g$, and $2E_r$, respectively. Next, Ref. [11] defined quasispecies in the form of n-stars, each of which is a given particle decorated by the n interparticle vector distances (edges) to its n neighbors (see for example Fig. 4). Each such edge is colored according to the spin orientations. We denote by i, j, and k the number of red, green, and blue edges such that $n = i + j + k$. It turns out that in the temperature range of interest $(0 < T < 0.5)$, in an overwhelming majority of n-stars (more than 98%), the central particle has a spin orientation that is favorable with respect to two of its edges, leading to the constraint (cf. [11])

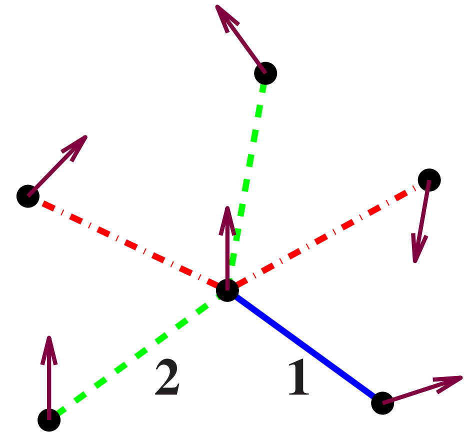

FIG. 4. (Color online) An example of an n-star with $n = 5$, $i = 2$, $j = 2$, and $k = 1$. The central particle has a spin with favored orientation with respect to edges 1 and 2. Thus these edges can be either blue or green, and this central spin cannot be favored with respect to any other edge. In the interesting range of temperatures we observe 36 n-stars with $4 \leq i + j + k \leq 6$. Colors are as used in Fig. 3.

$$\sum_{ijk} (j + 2k) c_{ijk} = 4, \tag{6}$$

where c_{ijk} is the concentration of n-stars with i, j, and k red, green, and blue edges, respectively. This constraint is important for the statistical mechanics of this system. The energy of an n-star (referred to as a quasiparticle) is computed as

$$E_{ijk} = iE_r + jE_g + kE_b, \tag{7}$$

where $k \leq 2$. Note that, since the energies on the right-hand side (RHS) of Eq. (7) depend on temperature, so does the energy of the quasiparticles. Notwithstanding, in the interesting temperature range the temperature dependence is weak; we take the energies of the quasiparticles as T independent. The degeneracy g_{ijk} of the energy level (number of quasiparticles with the same energy) was computed in [11] in the form

$$g_{ijk} = \binom{2}{k} \binom{i + j + k - 2}{i} 2^{j+2k-2} 4^{i-k+2}. \tag{8}$$

Finally we can write the partition function of the system:

$$Z[T, \lambda(T)] \equiv \sum_{ijk} g_{ijk} e^{-\beta E_{ijk}} e^{-\lambda(j+2k)}. \tag{9}$$

The Lagrange multiplier λ is introduced to ensure that the constraint (6) is satisfied. In terms of the partition function the mole fraction of quasiparticles is

$$c_{ijk} = \frac{g_{ijk} e^{-\beta E_{ijk}} e^{-\lambda(j+2k)}}{Z[T, \lambda(T)]}. \tag{10}$$

In [11] it was shown that the prediction of this formula agrees well with simulations until the system is “jammed,” or, more correctly, until the simulation time is too short to allow the system to equilibrate. Here we will use this theory

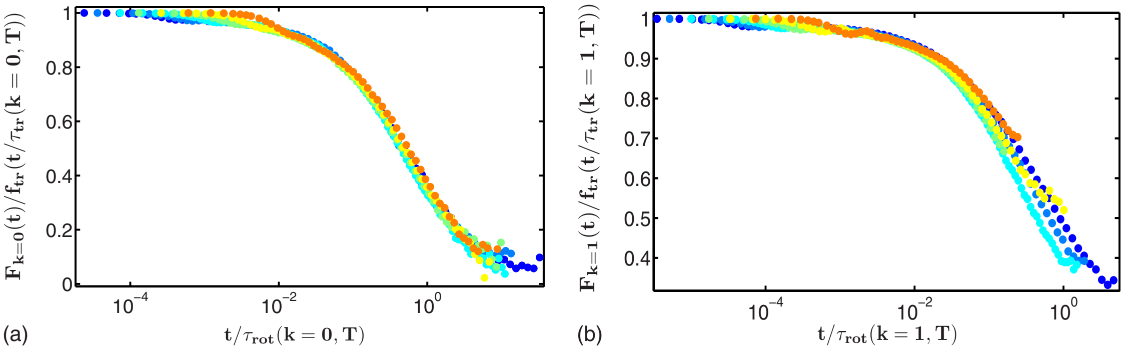

FIG. 5. (Color online) Test of data collapse to validate the assumption (12). All the temperature shown in Fig. 1 are employed in this test. Note that the data for the higher temperatures ($T=0.3$ and 0.25) do not contribute throughout the range of t/τ since the raw functions are already extremely small at long times.

to compute the spin-autocorrelation function. As noted in [11], we do not need to discuss separately all the 36 quasispecies, it suffices to bunch groups of c_{ijk} together into groups with $k=0,1,2$. Thus we will use the notation $c_k \equiv \Sigma_{ij} c_{ijk}$. This bunching is natural since it stresses the different environments (potential barriers for unit vector orientation) seen by the quasispecies in each group, helping us to disentangle the competing dynamics leading to relaxation.

III. ANALYSIS OF THE SPIN DECORRELATION

A. Elementary processes

We denote below the spin-relaxation function for each value of k as $F_k(t)$. This function is defined as in Eq. (5) but restricted to particles whose n-stars are characterized by $k=0$, 1, or 2,

$$F_k(t) \equiv (1/N_k)\sum_{i\in k} \langle \boldsymbol{u}_i(t)\cdot \boldsymbol{u}_i(0)\rangle, \qquad (11)$$

where N_k is the number of n-stars with a given value of k. We expect these functions to depend on k but not to change (as a function) with temperature. Next we note that a spin can change its angle with respect to an interparticle vector distance either due to the spin rotation with the interparticle vector distance fixed, or due to translation in which the interparticle vector distance changes (cf. [1], Fig. 6). We expect that the typical times for rotational and for translational relaxation may differ, and may also have different temperature dependence. We denote the rotational relaxation time as $\tau_{\rm rot}(k,T)$, providing it with temperature dependence and also with dependence on $k=0,1,2$. Similarly, the translational relaxation time is denoted $\tau_{\rm tr}(k,T)$. Finally, we present our main assumption (to be tested against the data) that to a good approximation these relaxation channels are independent and competing, allowing us to write the relaxation function $F_k(t)$ for each family of quasiparticles $k=0,1,2$ as a product of two scaling functions:

$$F_k(t) \approx f_{\rm rot}\left(\frac{t}{\tau_{\rm rot}(k,T)}\right) f_{\rm tr}\left(\frac{t}{\tau_{\rm tr}(k,T)}\right). \qquad (12)$$

We will show (see Fig. 5) that the *scaling functions* on the RHS of Eq. (12) do not depend on the temperature. Of course the typical relaxation times $\tau_{\rm rot}(k,T)$ and $\tau_{\rm tr}(k,T)$ may depend on time in a way that we should be able to model.

Modeling of the translation channel is the same for all the k groups, since the slowing down of translation in this system is dominated by the decrease in concentration of the $k=0$ quasispecies as the temperature decreases [11]. Indeed, with the concentration of $c_{k=0}(T)$ decreasing, one defines a typical increasing scale $\xi(T) \equiv 1/\sqrt{c_{k=0}(T)}$, whose physical meaning is the typical length of the cooperative event that results in any appreciable translational motion. Accordingly the typical relaxation time associated with translation grows as [2]

$$\tau_{\rm tr}(k,T) = \tau^0_{\rm tr}(k) e^{\mu\xi(T)/T}, \qquad (13)$$

where μ is the characteristic free energy per particle involved in the cooperative event of length ξ and $\tau^0_{\rm tr}$ is an attempt time (of the order of unity) that may depend on k.

At this point we note that in many instances where scaling theory prevails, it is much easier to determine theoretically the correlation scales or the relaxation times than to guess the scaling *functions*. The present problem is not an exception. We do not know at the present time how to determine the relaxation functions from pure thought, and we must ask the simulation for help. Thus, for example, we find from the data analysis that the relaxation function $f_{\rm tr}(t/\tau_{\rm tr}(k))$ is a simple exponential,

$$f_{\rm tr}(t/\tau_{\rm tr}(k,T)) = e^{-t/\tau_{\rm tr}(k,T)}, \qquad (14)$$

and all the non-Arrhenius dependence comes from the dependence of ξ on T. We stress that in other cases the scaling function might be a stretched exponential (see below), or any other legal scaling function as long as it depends on (t/τ) only.

The rotation channel calls for more scrutiny, since the $k=0$ and 1 quasispecies differ significantly from the $k=2$ quasispecies, as the latter tend to aggregate in clusters. We therefore need to deal with them differently. Quasiparticles with $k=0,1$ are relatively free to rotate, and all that they need to do is to overcome the potential energy barrier for rotation. We thus expect their relaxation times to be of simple Arrhenius form, i.e.,

TABLE I. Parameters used in the model.

	$k=0$	$k=1$	$k=2$
β	0.57	0.45	0.6
$\Delta E_{\mathrm{rot}}(k)$	1.27	1.33	
μ	0.27	0.32	0.39
$\tau^0_{\mathrm{rot}}(k)$	0.24	2.48	
$\tau^0_{\mathrm{tr}}(k)$	2.48	1.6	1.07

$$\tau_{\mathrm{rot}}(k) = \tau^0_{\mathrm{rot}}(k)e^{\Delta E_{\mathrm{rot}}(k)/T} \quad \text{for } k=0,1, \tag{15}$$

with $\Delta E_{\mathrm{rot}}(k)$ of the order of the energies of the "bonds" broken. This is indeed what is found (see Table I). The functional form of the rotational scaling function turns out to be stretched exponential, i.e.,

$$f_{\mathrm{rot}}(t/\tau_{\mathrm{rot}}(k,T)) \approx e^{-[t/\tau_{\mathrm{rot}}(k,T)]^{\beta(k)}} \quad \text{for } k=0,1, \tag{16}$$

with $\beta(k)$ that does not depend on the temperature. The values of these temperature-independent parameters are shown in Table I. These parameters are obtained from best fits of the presumed functional forms to the simulation data.

Since the assumption (12) appears new to the subject of glassy dynamics, we should test it very carefully. The best test is to divide, for each k value, the measured relaxation function $F_k(t)$ by either $f_{\mathrm{rot}}(t/\tau_{\mathrm{rot}}(k,T))$ or $f_{\mathrm{tr}}(t/\tau_{\mathrm{tr}}(k,T))$ and show that the remaining quantity is a scaling function of one variable as stated. In other words, we should show that we can get a convincing data collapse by plotting such ratios as a function of time scaled by the relaxation times, either (13) or (15) as is appropriate. In Fig. 5 (left panel) we show $F_{k=0}(t)/f_{\mathrm{tr}}(t/\tau_{\mathrm{tr}}(k=0,T))$ for all the different temperatures shown in Fig. 1. We see that, in spite of the considerable variation in orders of magnitude in the relaxation functions, the data collapse observed here as function of $t/\tau_{\mathrm{rot}}(k=0,T)$ is excellent indeed. In Fig. 5 (right panel) we show a similar data collapse for $k=1$. While not as superb as the data collapse for $k=0$, we still accept it as good enough in light of the huge dispersion of the original relaxation functions.

For $k=2$ we cannot expect such a simple model to hold. The reason is that at lower temperatures the $k=2$ quasiparticles aggregate inside clusters whose average size increases when the temperature decreases [6]. The distribution of cluster sizes depends on T, and to represent the rotational relaxation function one needs to decompose it into cluster contributions [9,10]. Each cluster may decay simply with Arrhenius decay time, but the ensemble is expected to show a strongly non-Arrhenius relaxation time, as shown in [9,10]. For the sake of brevity we do not attempt here to derive the rotational relaxation function of the $k=2$ quasiparticles but we simply measure and fit a relaxation function according to

$$f_{\mathrm{rot}}(t/\tau_{\mathrm{rot}}(k=2,T)) \approx \exp\{-[t/\tau_{\mathrm{rot}}(k=2,T)]^{0.6}\}, \tag{17}$$

with the measured value of $\tau_{\mathrm{rot}}(k=2,T)$ as shown in Fig. 6. Note that this relaxation function is again temperature independent [except through the dependence of $\tau_{\mathrm{rot}}(k=2)$].

We thus possess models for all the elementary relaxation functions in addition to Eq. (17). The parameters used are temperature independent, and are summarized in Table I. All that remains is to sum up the contributions together with the right weights.

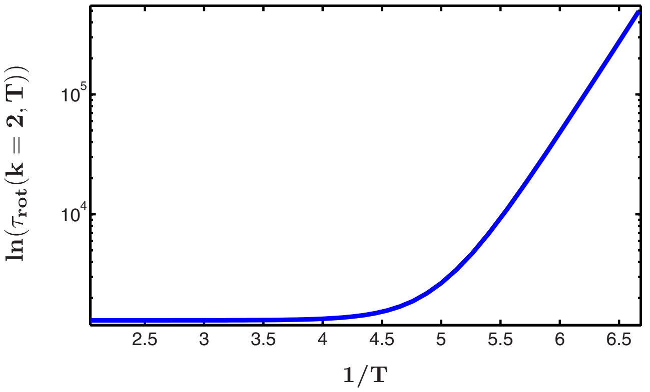

FIG. 6. (Color online) The logarithm of the relaxation time $\tau_{\mathrm{rot}}(k=2)$ as a function of inverse temperature.

B. Computing the correlation functions

Having modeled the spin-decorrelation formulas due to the two channels of decay for the three natural groups of quasiparticles, we should be able to predict the total relaxation function simply by summing up the three contributions, with each one weighted by the predicted concentration of the appropriate group of quasispecies with a given k. In other words, we should plot

$$C_R(t) = \sum_{k=0}^{2} c_k(T)F_k(t), \tag{18}$$

and compare the results with the data. This comparison is shown in Fig. 7. It is quite clear that the agreement is essentially perfect.

IV. CONCLUDING REMARKS

We reiterate that the functions $F_k(t)$ in Eq. (7) are products of scaling functions and are therefore temperature inde-

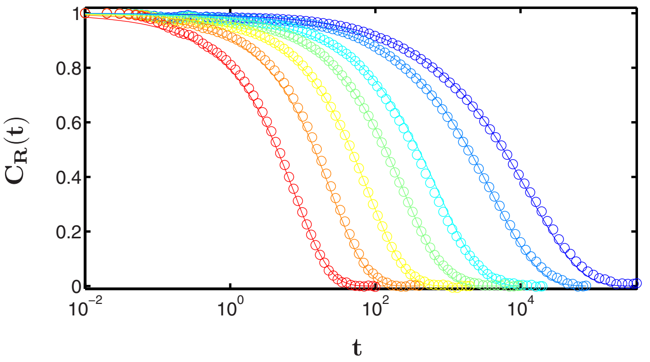

FIG. 7. (Color online) Comparison of the theoretical relaxation function (7) (circles) with data from the simulations (continuous line). The temperatures shown from left to right are $T=0.4$, 0.3, 0.25, 0.22, 0.20, 018, and 0.17.

pendent functions. All the temperature dependence in Fig. 7 stems from the dependence of the typical decay time of each elementary process and from the temperature-dependent weights of the concentrations of k groups of quasispecies. The apparent change of β in the stretched exponential fit to this data [6] as a function of temperature stems solely from the change of importance of the various k groups as a function of the temperature, and from the change of importance of rotation vs translation (remember that the translational elementary contributions appear here always as pure exponentials).

The bottom line of this analysis is twofold. First, we demonstrate that it is possible to break apart relaxation processes in glass-forming systems into more elementary contributions, giving much better a understanding of the origin of the complex time dependence of relaxation functions. In this point we simply extend what was proposed in [9,10]. Second, we stress the danger of straight numerical fits to relaxation functions; when these change their functional form with temperature, the reason should be sought in the existence of a composite process with various dynamical contributions, each of which may be quite simple. Fitting blindly an "overall" relaxation time to an "overall" relaxation function may yield relaxation times with an incorrect temperature dependence. Note that the analysis presented above exhibits some processes whose relaxation times are pure Arrhenius, and some whose relaxation times are super-Arrhenius. Is the glass-forming system then fragile or strong? We conclude that whether the system is fragile or strong in the Angell parlance [1] may be in the eyes of the beholder, especially if the said beholder did not reveal the details of the physical phenomenon. While it is easier to decompose the relaxation process into its physical components in numerical simulations, careful experiments that can follow single molecules [12] should be useful in clearing up the physical picture of glassy relaxation.

ACKNOWLEDGMENTS

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